23.5 KRONIG PENNEY MODEL

In the free electron theory it is assumed that the potential to which the valence electrons are subjected is constant and, therefore, it can be taken to be equal to zero, while solving Schrödinger's equation. But this is not true for the valence electron in ionic and co-valent crystalline solids because in such solids the electrons are localised near the parent nuclei. This gives rise to a periodically varying potential. Thus, in an actual case the constant potential should be replaced by a periodically varying potential.

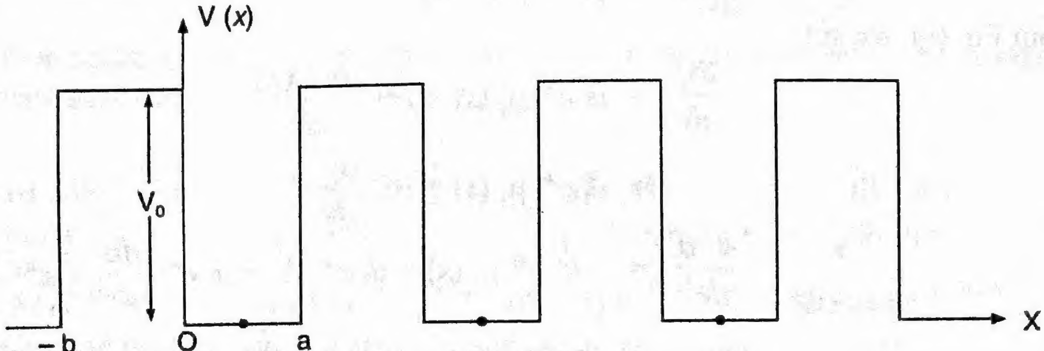

Fig. 23.7.

Kronig and Penney model illustrates the behaviour of electrons in a periodic potential by assuming a relatively simple one dimensional model of periodic potential as shown in Fig. 23.7, which shows the periodic potential energy of a valence electron in the X-direction.

Basic Assumptions

In Kronig Penney model it is assumed that the potential energy of an electron in a linear array of positive nuclei has the form of a periodic array of square wells with period $(a + b)$.

At the bottom of the well, *i.e.*, for $0 < x < a$ the electron is assumed to be in the vicinity of a nucleus and the potential energy is taken as zero, whereas outside a well, *i.e.*, for $-b < x < 0$ the potential energy is assumed to be V_0.

Analytical Treatment

Although this model employs a very crude approximation to the type of periodic potential existing inside a lattice, yet it is very useful to illustrate various important features of the quantum behaviour of the electron in the periodic lattice.

The Schrodinger's equations for the two regions are

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0 \quad \text{for} \quad 0 < x < a \qquad \text{... (i)}$$

and

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - V_0)\psi = 0 \quad \text{for} \quad -b < x < 0 \qquad \text{... (ii)}$$

We shall assume that the energy E of the electron under consideration is smaller than V_0 and define two real quantities α and β given by

$$\alpha^2 = \frac{2mE}{\hbar^2} \text{ and } \beta^2 = \frac{2m(V_0 - E)}{\hbar^2} \qquad \text{... (iii)}$$

Eqs. (*i*) and (*ii*) can now be written as

$$\frac{d^2\psi}{dx^2} + \alpha^2 \psi = 0 \quad \text{for} \quad 0 < x < a \qquad \text{... (iv)(a)}$$

and

$$\frac{d^2\psi}{dx^2} - \beta^2 \psi = 0 \quad \text{for} \quad -b < x < 0 \qquad \text{... (iv)(b)}$$

The potential is periodic, and is given by

$$V(x) = V(x + a + b)$$

where $(a + b)$ is the period.

Using Bloch theorem, the solution of wave equation for a periodic potential will be of the form of a plane wave modulated with the periodicity of the lattice and will be given by

$$\psi(x) = e^{ikx} \mu_k(x) \qquad \text{... (v)}$$

where $\mu_k(x)$ is the periodic function in x with period $(a + b)$, *i.e.*,

$$\mu_k(x) = \mu_k(x + a + b)$$

From Eq. (*v*), we get

$$\frac{d\psi}{dx} = ik\, e^{ikx} \mu_k(x) + e^{ikx} \frac{d\mu_k(x)}{dx}$$

$$= ik\, e^{ikx} \mu_k(x) + e^{ikx} \frac{d\mu}{dx} \qquad \text{... (vi)}$$

and

$$\frac{d^2\psi}{dx^2} = -k^2 e^{ikx} \mu_k(x) + ik\, e^{ikx} d\mu + ik\, e^{ikx} \frac{d\mu}{dx} + e^{ikx} \frac{d^2\mu}{dx^2}$$

$$= -k^2 e^{ikx} \mu_k(x) + 2ik\, e^{ikx} \frac{d\mu}{dx} + e^{ikx} \frac{d^2\mu}{dx^2} \qquad \text{... (vii)}$$

Substituting the values of $\psi(x)$ from Eq. (v) and $\frac{d^2\psi}{dx^2}$ from Eq. (vii) in Eqs. (iv) (a) and (iv) (b), we get

$$-k^2 e^{ikx}\mu + 2ik\, e^{ikx}\frac{d\mu}{dx} + e^{ikx}\frac{d^2\mu}{dx^2} + \alpha^2 e^{ikx}\mu = 0$$

(In the above Equation instead of $\mu_k(x)$, we have used μ only)

or
$$\frac{d^2\mu}{dx^2} + 2ik\frac{d\mu}{dx} + (\alpha^2 - k^2)\mu = 0 \qquad \text{... } (viii)$$

for
$$0 < x < a$$

and
$$\frac{d^2\mu}{dx^2} + 2ik\frac{d\mu}{dx} - (\beta^2 + k^2)\mu = 0 \qquad \text{... } (ix)$$

for
$$-b < x < 0$$

The solutions of these equations are

$$\mu_1 = A\, e^{i(\alpha - k)x} + B\, e^{-i(\alpha + k)x} = 0 \qquad \text{... } (x)$$

for
$$0 < x < a$$

and
$$\mu_2 = C\, e^{(\beta - ik)x} + D\, e^{-(\beta + ik)x} = 0 \qquad \text{... } (xi)$$

for
$$-b < x < 0$$

Where A, B, C and D are constants.

These constants must be chosen in such a manner that the following boundary conditions are satisfied, *i.e.*, the wave function ψ and its derivative $\frac{d\psi}{dx}$ are single valued and continuous

$$\therefore \quad (\mu_1)_{x=0} = (\mu_2)_{x=0};\quad \left(\frac{d\mu_1}{dx}\right)_{x=0} = \left(\frac{d\mu_2}{dx}\right)_{x=0} \qquad \text{... } (xii)$$

and
$$(\mu_1)_{x=a} = (\mu_2)_{x=a};\quad \left(\frac{d\mu_1}{dx}\right)_{x=a} = \left(\frac{d\mu_2}{dx}\right)_{x=b} \qquad \text{... } (xiii)$$

The first two conditions are imposed because of the requirement of continuity and the other two conditions are required because of periodicity of $\mu_k(x)$.

The application of these boundary condition to Eqs. (x) and (xi), gives

$$A + B = C + D$$

$$A\, i(\alpha - k) - B\, i(\alpha + k) = C(\beta - ik) - D(\beta + ik)$$

$$A\, e^{i(\alpha - k)a} + B\, e^{-i(\alpha + k)a} = C\, e^{-(\beta - ik)b} + D\, e^{(\beta + ik)b}$$

$$Ai(\alpha - k)\, e^{i(\alpha - k)a} - B\, i(\alpha + k)\, e^{-i(\alpha + k)a} = C(\beta - ik)\, e^{-(\beta - ik)b} - D(\beta + ik)\, e^{(\beta + ik)b}$$

These four equations have a non-zero solution only if the determinant of the coefficients A, B, C and D vanishes, *i.e.*,

$$\begin{vmatrix} 1 & 1 & 1 & 1 \\ i(\alpha - k) & -i(\alpha + k) & (\beta - ik) & -(\beta + ik) \\ e^{i(\alpha - k)a} & e^{-i(\alpha + k)a} & e^{-(\beta - ik)b} & e^{(\beta + ik)b} \\ i(\alpha - k)\, e^{i(\alpha - k)a} & -i(\alpha + k)\, e^{-i(\alpha + k)a} & (\beta - ik)\, e^{-(\beta - ik)b} & -(\beta + ik)\, e^{(\beta + ik)b} \end{vmatrix} = 0$$

On solving the determinant and after simplification, we obtain

$$\frac{\beta^2+\alpha^2}{2\beta\alpha}\sinh\beta b\sin\alpha a+\cosh\beta b\cos\alpha a=\cos k\,(a+b) \qquad \text{... (xv)}$$

To simplify this equation Kronig and Penney considered the case when $V_0 \to \infty$ and $b \to 0$, but the product $V_0 b$ has a finite value, *i.e.*, the potential barriers become *delta* functions. Under these conditions the model is modified in such a way that it represents a series of wells separated by infinitely thin potential barriers of infinitely large potential. The limiting value of $V_0 b$ for $V_0 \to \infty$ and $b \to 0$ is known as *barrier strength.*

As $\quad b \to 0$, $\sinh\beta b \to \beta b$ and $\cosh\beta b \to 1$.

Also from Eq. (*iii*),

$$\beta^2+\alpha^2 = \frac{2mV_0}{\hbar^2}$$

or

$$\frac{\beta^2+\alpha^2}{2\alpha\beta} = \frac{mV_0}{\alpha\beta\hbar^2}$$

$\therefore$ Eq. (*xv*) becomes

$$\frac{mV_0}{\alpha\beta\hbar^2}\beta b\sin\alpha a+\cos\alpha a=\cos ka$$

$$\left[\frac{mV_0 b}{\alpha\hbar^2}\right]\sin\alpha a+\cos\alpha a=\cos ka \qquad \text{... (xvi)}$$

Let us now define a quantity $P=\dfrac{mV_0 ba}{\hbar^2}$, which is a measure of the area $V_0 b$ of the potential barrier.

$$\therefore \qquad P\frac{\sin\alpha a}{\alpha a}+\cos\alpha a=\cos ka \qquad \text{... (xvii)}$$

The physical significance of the quantity P is that if P is increased the area of the potential barrier is increased and the given electron is bound more strongly to a particular potential well. When $P \to 0$, the potential barrier becomes very weak which mean that electrons are *free electrons.* In this case we obtain from Eq. (*xvii*)

$$\alpha a = ka \quad \text{or} \quad \alpha = k$$

Now,

$$\alpha^2 = \frac{2mE}{\hbar^2} = k^2 \qquad \text{... (xviii)}$$

Hence,

$$E = \frac{k^2\hbar^2}{2m} = \frac{h^2k^2}{8\pi^2 m} \qquad \text{... (xviii)(a)}$$

This result is the same as obtained by the free electron model. Equation (*xvii*) also gives the condition which must be satisfied so that solutions of the wave equation may exist. Since $\cos k\alpha$ lies between + 1 and – 1, the left hand side [of Eq. (*xvii*)] should take up only those values of αa for which its values lie between + 1 and – 1. Such values of αa, therefore, represent wave like solutions of the form

$$\psi(x) = e^{ikx}\mu_k(x)$$

and are *allowed values*. The other values of αa are *not allowed.*

If we plot a graph between $\left(\dfrac{P\sin\alpha a}{\alpha a}+\cos\alpha a\right)$ and αa for the value of $P=\dfrac{3\pi}{2}$, we get the curve shown in Fig. 23.8.

From Eq. (*xviii*) $\alpha = \sqrt{\dfrac{2mE}{\hbar^2}}$. Therefore, the abscissa is a measure of energy and by finding the value of αa at any point the energy represented by the function at that point is calculated. The values of αa satisfying the equation

$$P\frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka$$

are obtained by drawing lines parallel to αa –axis at a distance $\cos ka$ from it and if ka is continuously varied from 0 to π, *i.e.*, $\cos ka$ from + 1 to – 1, we obtain all possible values of αa and hence that of energy can be calculated. These possible values of αa are shown by thick lines.

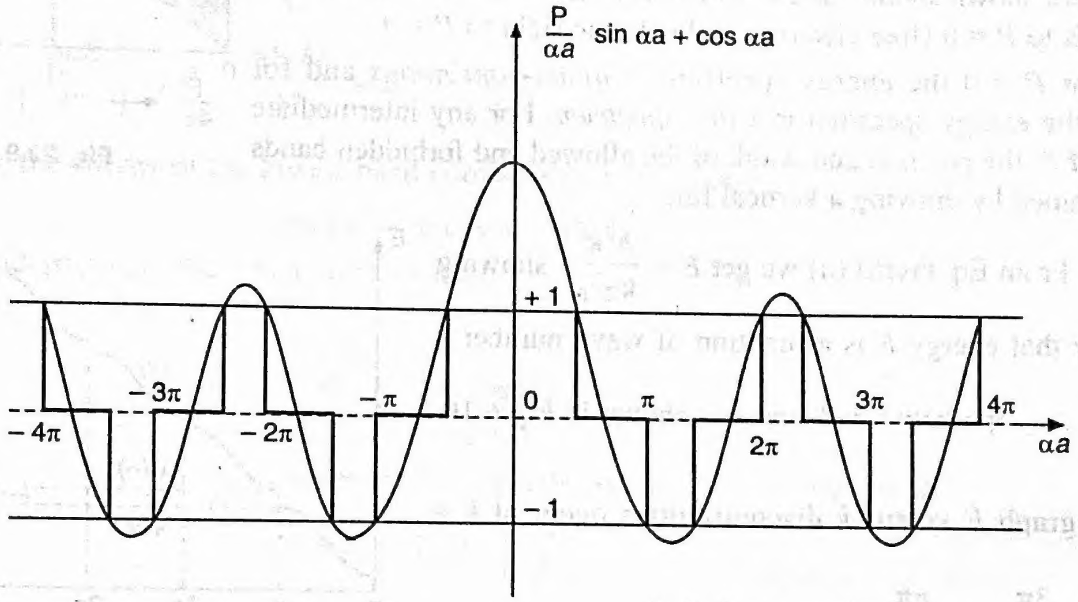

Fig. 23.8

From Fig. 23.8, the following conclusions are drawn:

Conclusions. 1. *Allowed and forbidden energy bands*. The energy spectrum consists of an infinite number of *allowed energy bands* (shown thick) separated by intervals in which there are no energy levels (shown dotted). These are known as *forbidden regions* or *bands*.

The boundaries of the allowed energy levels correspond to the values of $\cos ka = \pm 1$

or $$ka = n\pi \quad \text{or} \quad k = \frac{n\pi}{a}$$

2. As αa increases the term $P\dfrac{\sin \alpha a}{\alpha a}$ on the left hand side of Eq. (*xvii*) decreases so that width of allowed energy bands increases and hence forbidden energy regions become narrower.

3. The width of allowed energy bands decreases with the increasing value of P (*i.e.*, with the increasing binding energy of the electron). When $P \to \infty$, the allowed energy bands become infinitely narrow and are independent of k, *i.e.*, energy spectrum becomes a line spectrum.

When $P \to \infty$ the allowed energy ranges of αa reduces to points given by

$$\alpha a = \pm n\pi$$

or $$\alpha^2 = \frac{n^2\pi^2}{a^2} = \frac{2mE}{\hbar^2}$$

$\therefore$ $$E = \frac{n^2\pi^2\hbar^2}{2ma^2} \qquad \text{... (xix)}$$

From Eq. (*xix*), we find that E is independent of k. The energy levels in this case are discrete and the electron is completely bound, *i.e.*, the electrons remain within the potential wells and move only in one cell of width a. This case applies to crystals where the electrons are tightly bound to their nuclei.

If P is small, the barrier strength is small and in the limit $P \to 0$ (no barrier) the electron can be considered to be moving freely through the potential well. This case applies to crystals where the electrons are almost free of their nuclei. The effect of varying P on the band structure is shown in Fig. 23.9. Allowed and forbidden energy ranges are shown *shaded* and *open* respectively. The extreme left corresponds to $P = 0$ (free electron) and extreme right to $P = \infty$.

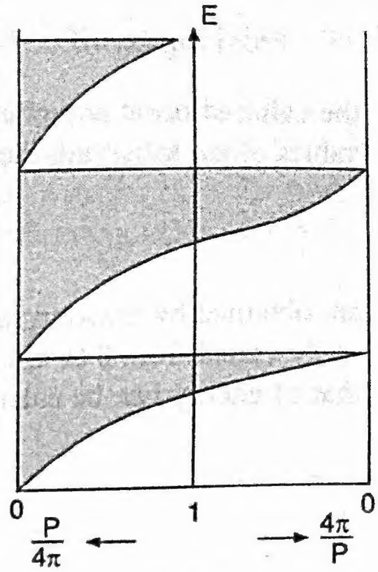

Fig. 23.9.

For $P = 0$ the energy spectrum is *quasi-continuous* and for $P = \infty$ the energy spectrum is a *line spectrum*. For any intermediate value of P, the position and width of the allowed and forbidden bands are obtained by drawing a vertical line.

4. From Eq. (*xviii*) (*a*) we get $E = \dfrac{h^2k^2}{8\pi^2 m}$ showing thereby that energy E is a function of wave number k $\left(\dfrac{2\pi}{\lambda}\right)$. A graph between E and k is shown in Fig 6.10.

In the graph E versus k discontinuities occur at $k = \dfrac{\pi}{a}, \dfrac{2\pi}{a}, \dfrac{3\pi}{a}, \ldots\ldots, \dfrac{n\pi}{a}$ where $n = 1, 2, 3, \ldots\ldots$

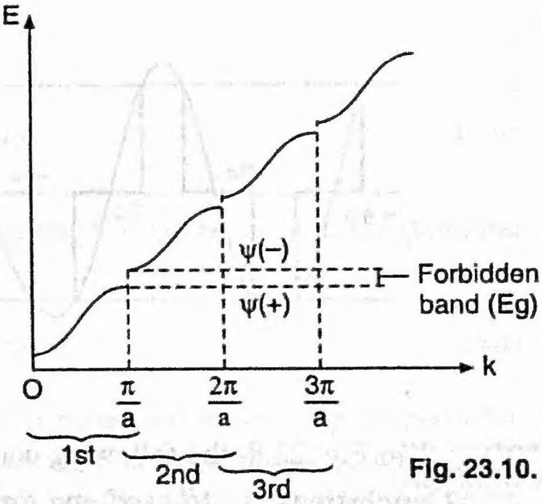

Fig. 23.10.

The k values define the first, second, third etc., *Brillouin Zones*. For $k = +\dfrac{\pi}{a}$ to $-\dfrac{\pi}{a}$, there exists the first Brillouin Zone. The second Brillouin zone consists of two parts, from $+\dfrac{\pi}{a}$ to $+\dfrac{2\pi}{a}$ and the second from $-\dfrac{\pi}{a}$ to $-\dfrac{2\pi}{a}$. Each portion of the curve may be called a *band*. The curves are

(*i*) horizontal at the top and the bottom

(*ii*) parabolic near the top and the bottom with curvature in opposite directions

(*iii*) $\dfrac{d^2E}{dk^2}$ is positive in the lower portion of the band and negative in the upper portion.

(*iv*) The zone boundaries represents the maximum energies that the electron can have without any discontinuity.

(*v*) Within a given energy band, the energy is a periodic function of k. For, example, if we replace k by $k + \dfrac{2\pi n}{a}$, where n is an integer in the right hand side of equation

$$P\,\frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka$$

the equation remains the same because $\cos\left(k + \dfrac{2\pi n}{a}\right)a = \cos(ka + 2\pi n) = \cos ka$.

Velocity of Electron

As per de Broglie's theory, wave packet is associated with moving electron and the group velocity v_g of the wave packet is same as that of velocity of electron

$$v = v_g = \frac{d\omega}{dk}$$

We also know that the energy associated with electron is

$$E = \hbar\omega$$

Hence, the velocity $$\vec{v} = \frac{d\omega}{dk} = \frac{1}{\hbar}\frac{dE}{dk}$$

$$= \frac{1}{\hbar} \text{ (slope of } E \text{ versus } k \text{ graph)}$$

The changes in the energy corresponding to wave vector $\vec{k}$ of electrons in Kronig-Penny model is shown in Fig. 6.7. The slope of $E - k$ curve in the graph at the top and bottom is, so the velocity of electron at the top and bottom is also zero. The slope is maximum at $k = k_0$, therefore the velocity of electron is also maximum at $k = k_0$. The point where the slope of E versus k graph is maximum is known as point of inflexion.

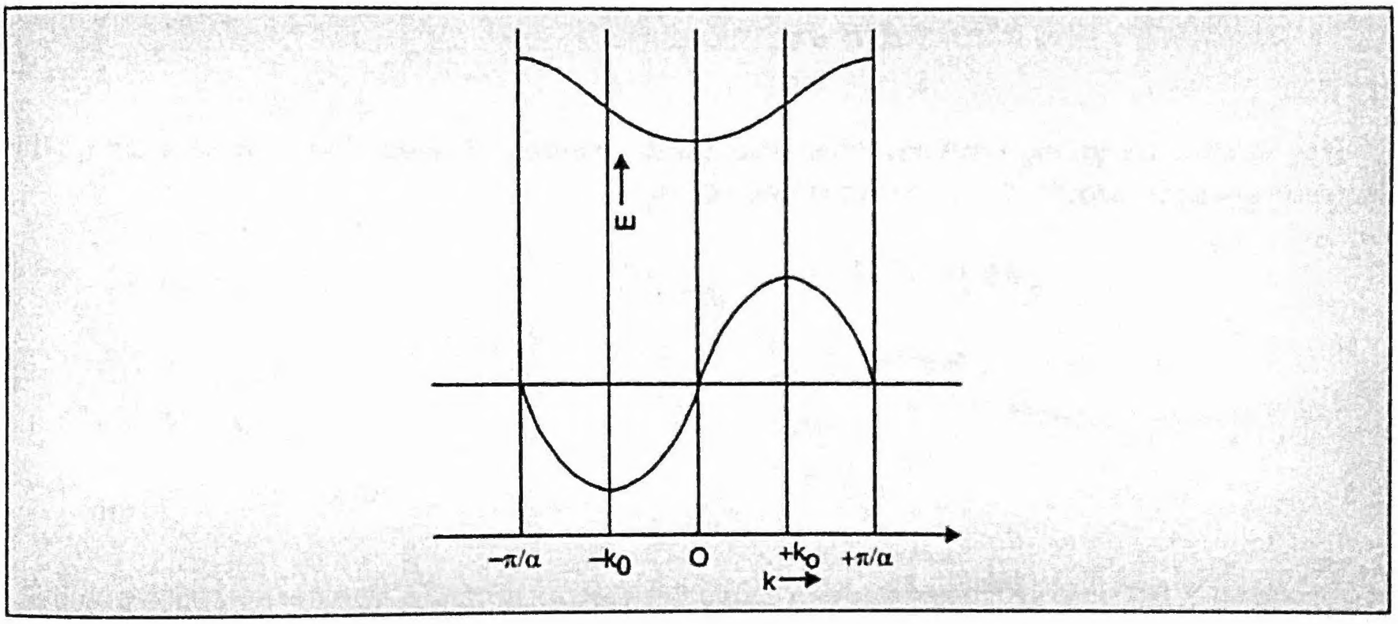

Fig. 6.7

When electron is free, then there is no energy band and the energy corresponding to free electron is expressed as

$$E = \frac{\hbar^2 k^2}{2m}$$

Hence $$\vec{v} = \frac{1}{\hbar}\frac{dE}{dk} = \frac{\hbar k}{m} = \frac{p}{m}$$

If we plot a graph between velocity of electron and wave vector $\vec{k}$, then the graph indicates that velocity increases linearly with $\vec{k}$ (Fig. 6.8).

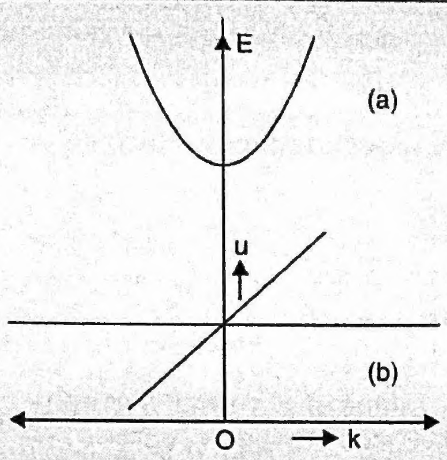

Fig. 6.8

Effective Mass of Electron

The acceleration of the electron moving in an external electric field ξ is given by

$$a = \frac{d}{dt}(v) \text{ where } v \text{ is the velocity of electron.}$$

$$= \frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{dk}{dt} \qquad \left(\because v = \frac{1}{\hbar}\frac{dE}{dk}\right)$$

If q is the charge on electron, then the small amount of work done dE in moving the electron by displacement dx by external force $q\xi$ is

$$dE = (q\xi)\,dx = (q\xi)\,\frac{dx}{dt} \times dt$$

$$= q\,\xi\,v_g\,dt$$

$$= q\,\xi\left(\frac{1}{\hbar}\frac{dE}{dk}\right)dt$$

or $$\frac{dk}{dt} = \frac{q\xi}{\hbar}$$

Hence, acceleration $$a = \frac{q\xi}{\hbar^2}\frac{d^2E}{dk^2}$$

or $$q\xi = \left[\frac{\hbar^2}{(d^2E/dk^2)}\right]a$$

The effective mass (m_{eff}) of vibrating electron in the crystal is

$$m_{eff} = \frac{\hbar^2}{d^2E/dk^2} \qquad \left(\because \frac{q\xi}{a} = \text{mass}\right)$$

Point to Remember

Effective mass of electron in a crystal is in inversely proportional to d^2E/dk^2.

The graph between kinetic energy E with respect to wave vector $\vec{k}$ is shown in Fig. 6.9.

At $\qquad k = \pm \frac{\pi}{a}$, E is maximum

$$\therefore \qquad \frac{d^2E}{dk^2} = -ve$$

At $k = k_0$, the slope of E versus k graph is maximum,

$$\therefore \qquad \frac{d^2E}{dk^2} = 0$$

Therefore, in the region between $\left(-\frac{\pi}{a}\right)$ to $-k_0$ and between k_0 to $\left(\frac{+\pi}{a}\right)$, the value of $\frac{d^2E}{dk^2}$ is negative

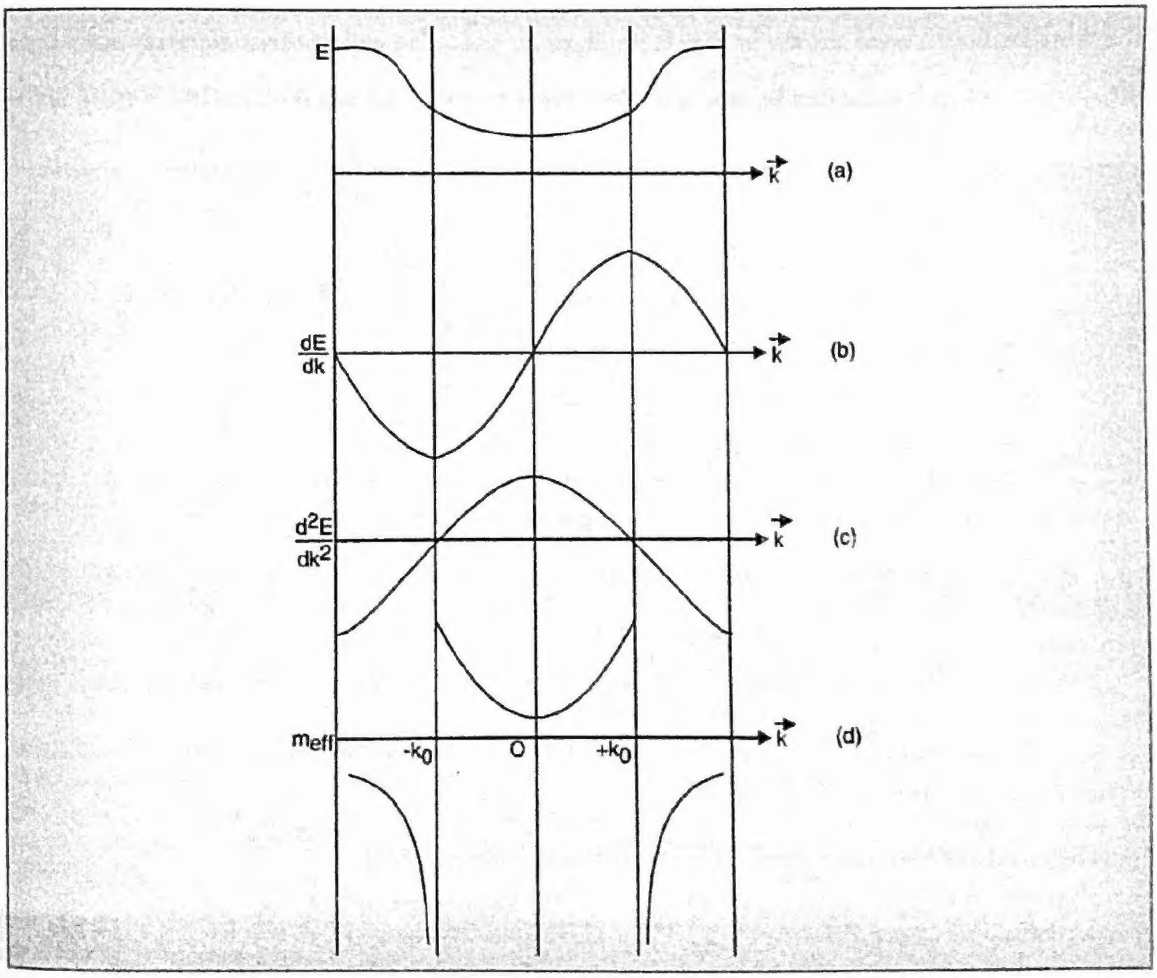

Fig. 6.9

(*viii*) When the effective mass is greater than the normal mass of the electron, then the electron is being bounded with lattice. The effective mass will be more if the binding is strong.

When effective mass is infinite at $k = \pm k_0$, it means that at given value of k, the electron is strongly bounded with lattice. The negative value signifies Bragg's reflection at Brillouin zone boundaries.

Energy of lowest energy band

According to Kronig Penney model the solution of Schrödinger's equation for one dimensional periodic lattice is given by

$$\frac{P \sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka$$

where $\alpha = \left(\frac{2mE}{\hbar^2}\right)^{1/2}$, $P = \frac{mV_0 ba}{\hbar^2}$ and $k = \pm \frac{n\pi}{a}$

Thus, the energy of the lowest band corresponds to $n = 1$ or $k = \pm \frac{\pi}{a}$

or
$$\cos ka = \pm \cos \pi = \pm 1$$

Considering only the magnitude, we have

$$\frac{P \sin \alpha a}{\alpha a} + \cos \alpha a = 1$$

or
$$\frac{P}{\alpha a} = \frac{1 - \cos \alpha a}{\sin \alpha a} \quad \text{... (i)}$$

Now,
$$\cos 2\theta = 1 - 2\sin^2\theta \quad \text{or} \quad 1 - \cos 2\theta = 2\sin^2\theta$$

$\therefore$
$$1 - \cos \alpha a = 2\sin^2\left(\frac{\alpha a}{2}\right)$$

and
$$\sin 2\theta = 2 \sin\theta \cos\theta$$

$\therefore$
$$\sin \alpha a = 2 \sin\left(\frac{\alpha a}{2}\right) \cos\left(\frac{\alpha a}{2}\right)$$

Substituting in (*i*), we have

$$\frac{P}{\alpha a} = \frac{2\sin^2\left(\frac{\alpha a}{2}\right)}{2\sin\left(\frac{\alpha a}{2}\right)\cos\left(\frac{\alpha a}{2}\right)} = \tan\left(\frac{\alpha a}{2}\right)$$

Since $P \ll 1$,
$$\frac{P}{\alpha a} = \tan\left(\frac{P}{\alpha a}\right), \text{ for lowest energy band}$$

$\therefore$
$$\tan\left(\frac{\alpha a}{2}\right) = \tan\left(\frac{P}{\alpha a}\right)$$

or
$$\frac{\alpha a}{2} = \frac{P}{\alpha a}$$

or
$$\alpha^2 = \frac{2P}{a^2}$$

But $\alpha^2 = \frac{2mE}{\hbar^2}$

$\therefore$
$$\frac{2P}{a^2} = \frac{2mE}{\hbar^2}$$

or
$$E = \frac{P}{ma^2}\hbar^2$$

This gives the energy of lowest energy band.